Chapter 7

Thermodynamic Sustainability Assessment of Biofuel Production from Oil Palm Biomass

Abstract In reality, all production processes proceed with the generation of entropy and destruction of useful energy of resource inputs. In view of this, the second law of thermodynamics can be directly linked with sustainability and sustainable development. Estimation of a system's exergy status in order to know the distribution of energy and matter, especially emissions, would help identify the efficiency of the system, hence improving it for sustainable development. In this chapter, the thermodynamic sustainability of biodiesel, bioethanol, biogas, and briquettes production from oil palm biomass are investigated via exergy analysis. Most studies on exergy analysis of biofuels production systems do not consider the production of the feedstocks though these stages are materials and energy intensive. The production of oil palm biomass for palm biofuels is assessed for thermodynamic feasibility in this study in order to give a complete overview of the contributions of every single unit within the palm biofuels production systems. Aspen Plus software was used for the mathematical modeling for all the case studies considered in this chapter. Potential causes and improvement options are also discussed in this chapter for sustainable palm biofuels production.

Keywords Thermodynamic sustainability · Palm biofuels · Oil palm biomass · Oil palm wastes · Biofuels exergy · Thermodynamic efficiency · Irreversibility · Palm biodiesel · Bioelectricity · Palm bioethanol · Exergy

7.1 Introduction

Energy is the driving force of almost all economies of the world thus, energy efficiency in production is important for sustainable development. The responsible production and consumption of biofuels must take into account issues of resource availability (exergy) and utilization, economic investment, and environmental impacts. Thermodynamic efficiency assessment combines both the economic and

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environmental aspects of sustainability (Valero et al. 1986) to give a clearer view of how energy is utilized during a process. Thermodynamic sustainability assessment is carried out using tools like energy and exergy analyses. More advanced tools like thermoeconomic analysis, exergoeconomic analysis, exergetic life cycle assessment, etc., could be used to assess the thermodynamic sustainability of production systems. The simultaneous use of the first and second laws of thermodynamics is applied to describe the quality and quantity of energy as well as its depletion rate within a system (Bejan et al. 1996; Fiorini and Sciubba 2005). When a system is assessed in terms of thermodynamic sustainability, the primary causes of its inefficiencies and the cost of obtaining the system's internal flows are established in a more comprehensive manner (Ayres et al. 2007; De Swaan et al. 2004).

The thermodynamic sustainability assessment tool, exergy, has been beneficial to the new engineering paradigm shift toward sustainable bioenergy development. Exergy helps to articulate the amount of resources that is consumed in any industrial process by quantifying the exergy losses in each unit operation. Exergy is a measure of the ability to perform work and higher exergy efficiencies are attained for processes in which exergy is less destroyed.

Thermodynamic or exergy analysis has been applied to biofuels production systems for sustainability assessment. The production of biohydrogen from biomass (Abuadala et al. 2010), biodiesel from used cooking oil (Talens et al. 2010), biodiesel from palm oil (Jaimes et al. 2010), bioethanol from sugarcane bagasse (Ojeda et al. 2011), biogas from brewer's spent grain (BSG) (Martin and Parsapour 2012), dimethyl ether from biomass (Zhang et al. 2009), biomethanol from sewage sludge (Ptasinski et al. 2002), oil palm fronds pretreatment systems for bioethanol production (Ofori-Boateng and Lee 2013), etc., have been assessed in terms of thermodynamic sustainability via exergy analyses. These studies address irreversibilities as main causes of exergy loss due to high heat transfer across high temperature difference resulting from the use of high quality exergy resources such as fossil fuel. Thermodynamic properties of streams in biofuels production systems for exergy calculations have been easily attained with the help of computer aided software like Aspen Plus (Dhar and Kirtania 2009; Doherty et al. 2010; Pellegrini and Silvio de Oliveira 2007), HYSYS (West et al. 2008), etc.

The cultivation of oil palm, palm oil milling, and conversion of palm biomass into biofuels make use of high-energy content resources like fossil fuel, which could affect the thermodynamic sustainability of the system. Though palm oil is the most consumed vegetable oil in the world today, its production processes have not been assessed in terms of exergy in order to improve yield and make it more economical. Because palm oil is the cheapest source of vegetable oil, it is gradually becoming one of the high biofuel feedstock alternatives. This chapter focuses on the degree of exergy destruction in palm biofuels production systems in order to assess their thermodynamic efficiencies for sustainable development. Process improvement options are also elaborated in this chapter.

7.2 Energy, Entropy, and Exergy: Comparative Overview

According to the first law of thermodynamics, energy can neither be created nor destroyed but conserved for all processes. This actually means that energy can never be consumed in a process which in fact is not logical considering irreversible processes in real situations. For instance, during heat transfer between a medium and its surrounding, there comes a specific time where the medium reaches the dead state,[1] where there is no extra heat exchange because the exergy content by then has been completely destroyed but no energy has been consumed.[2] At the dead state, the conditions of mechanical (the pressure), thermal (temperature), and chemical (chemical potentials) equilibria between the system and the environment are satisfied (Utlu and Hepbasli 2007). Because the conditions of the system are equal to those of the environment, the system has no motion or elevation relative to coordinates in the environment. Under these conditions, there is neither possibility of a spontaneous change within the system or the environment nor an interaction between them. The amount of resource that enters a process does not come out the same due to entropy generations within the system that has caused certain part of the resource to be consumed. Exergy is the quantity that can be consumed in processes and not energy hence, energy analysis though helpful may not actually quantify the quality of resource available to perform work which in fact, exergy analysis does. Sustainability emphasizes more on resource quality hence the need to quantify resources in terms of exergy in order to ascertain the degradation rate during a production process.

Energy as a physical quantity is dependent on only the characteristics of matter or energy flows but independent of environmental properties. This implies that energy balance does not quantify the usefulness or quality of a resource or provide information on resource destruction in a process (Sorguven and Ozilgen 2010). However, exergy analysis combines the first and second laws of thermodynamics to quantify the useful portion of energy that produces work (Peralta et al. 2010). Exergy of a resource is that part of the available energy which is fully convertible to other forms of energy.

Exergy can also be defined as the maximum theoretical useful work obtainable when a system is brought into thermodynamic equilibrium with its surrounding whereby there exist interactions between the system and environment (Wall 2010; Sciubba and Wall 2007).

Exergy analysis is also a thermodynamic sustainability tool that can be applied in quantifying emissions and wastes streams from a process (De Meester et al. 2006; Hermann 2006) as it is always measured based on a reference environment.

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[1] In a dead state system, the exergy of the stream or system is always zero due to the attainment of equilibrium with the reference environment (Ahrendts 1980).

[2] This makes the use of the phrase ‘energy consumption’ so ambiguous in that energy can never be destroyed according to the first law of thermodynamics. What is actually consumed is exergy hence, ‘exergy consumption.’

In a system where the work efficiencies of biofuels and their production systems are compared to fossil fuels, exergy analysis presents a better assessment tool in identifying their 'exergy efficiencies' and impacts on the environment (Talens et al. 2007; Ptasinski et al. 2007; Peralta et al. 2010).

Exergy quantifies the effect of energy and matter dissipation (entropy) while entropy quantifies the state of dispersion, i.e., the degree to which energy and matter are dispersed in a process which is nonideal or irreversible (Dewar 2005; Olawale and Adefila 1998).

7.3 Components of Exergy

Exergy may have components like physical ($\mathrm{Ex_{ph}}$), chemical ($\mathrm{Ex_{ch}}$), kinetic ($c^2/2$),[3] potential (gx),[4] and nuclear ($\mathrm{Ex_{nu}}$) exergies depending on the type of system under consideration (Szargut 2005; Carnot 1978; Kotas 1985). For instance, in a system which involves heat, work, and material transfers, the kinetic, potential, and nuclear exergies are not accounted for.

The *physical* or *thermo-mechanical* exergy of a system consists of mechanical exergy which depends on the system's pressure; and thermal exergy which also depends on the system's temperature (Carnot 1978; Szargut et al. 1988). According to Szargut et al. (1988), Eq. (7.1) mathematically defines physical exergy as:

$$\mathrm{Ex_{ph}} = (H - H_0) - T_0(S - S_0) \tag{7.1}$$

where $(H - H_0)$ and $(S - S_0)$ are the enthalpy change and entropy change of the system, respectively, at an environmental temperature of T_0 (298.15 K) and pressure P_0 (1 atm). The physical exergy of a system varies mathematically depending on the type of interactions occurring in the system. Equations 7.2 and 7.3 mathematically represent physical exergies of a perfect gas system (with constant specific isobaric heat capacity); and perfect solid and liquid systems (with constant specific heat capacity), respectively (Szargut et al. 1988):

$$\mathrm{Ex_{ph}} = c_p\left\{(T - T_0) - T_0 \,\mathrm{In}\frac{T}{T_0}\right\} + RT_0 \,\mathrm{In}\frac{P}{P_0} \tag{7.2}$$

$$\mathrm{Ex_{ph}} = \left\{(T - T_0) - T_0 \,\mathrm{In}\frac{T}{T_0}\right\} - v_m(P - P_0) \tag{7.3}$$

where $\mathrm{Ex_{ph}}$ is the physical exergy, c_p is the specific heat capacity, v_m is the specific volume at temperature T_0 (298.15 K), T is the temperature of the system, R is the gas constant (8.314 4621 J/mol/K), P is the system's operating pressure, and P_0 is the initial pressure (1 atm).

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[3] c is the velocity relative to Earth's surface.

[4] g is the constant of gravitational acceleration and x is the height.

Chemical exergy is the maximum net useful work obtained when a pure substance or working fluid into complete thermodynamic equilibrium with its environment of known chemical composition upon interactions in a system (Szargut et al. 1988). The chemical exergy of a material stream is the difference in the chemical potentials of the pure process components and the reference environment components in their environmental concentrations at their environmental conditions ($T_0 = 298.15$ K, $P_0 = 1$ atm) (Sato 2004). Chemical exergy is the most important exergy contribution to the overall exergy value of most natural resources like palm fruits. Equation 7.4 defines chemical exergy mathematically as:

$$\mathrm{Ex}_{\mathrm{ch},i} = \Delta G_f^o + \sum_k N_k \mathrm{Ex}^0_{\mathrm{ch},k} \tag{7.4}$$

where $\mathrm{Ex}_{\mathrm{ch},i}$, N_k, ΔG_f^o, and $\mathrm{Ex}^0_{\mathrm{ch},k}$ represent chemical exergy, number of moles of the kth reference species, Gibb's free energy of formation of the reference reaction, and the standard chemical exergy of the kth reference species, respectively.

The exergy of a steam is therefore found from Eq. 7.5:

$$\mathrm{Ex}_{\mathrm{system}} = \mathrm{Ex}_{\mathrm{ch}} + \mathrm{Ex}_{\mathrm{ph}} + \mathrm{Ex}_{\Delta\mathrm{mix}} \tag{7.5}$$

where $\mathrm{Ex}_{\Delta\mathrm{mix}}$ is the exergy of mixing of the system also mathematically defined by Eq. 7.6 (Szargut et al. 1988; Ayres and Ayres 1998):

$$\mathrm{Ex}_{\Delta\mathrm{mix}} = H_{\Delta\mathrm{mix}} - T_0 S \Delta\mathrm{mix}[T, P] \tag{7.6}$$

where $H_{\Delta\mathrm{mix}}$ is the enthalpy of mixing.

In this chapter, the exergy of mixing is assumed to be part of the physical exergy.

7.3.1 Exergy Destruction and Exergy Efficiency

Due to chemical reactions and other physical interactions between molecules in a system,[5] real processes are irreversible (Rivero 2002; Wall 2010) and some part of the total exergy of the interacting resources degrade during the process. This degradation results in low exergy output compared to the input exergy. This destroyed exergy due to entropy generation is often referred to as the *internal or endogenous exergy destruction* (Rivero et al. 1999; Rucker and Gruhn 1999). Irreversibility in a system is caused by lack of thermodynamic equilibrium and the dissipative effects associated with a natural process which leads to entropy generation and process inefficiencies. The exergy destroyed due to entropy generation in a system is unavoidable but can be minimized to some extent through various means which are discussed in this chapter. In energy conversion systems like biofuels production, the extent of exergy destruction is caused by equipment inefficiencies and energy value of resources entering the system. The endogenous exergy destruction of a system does not depend on the changes in the exergy destruction within the remaining components hence it gives accuracy to the performance of the system (Tsatsaronis et al. 2006).

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[5] Examples of interactions in a system which lead to irreversibilities are heat and momentum transfers through a finite temperature difference, mixing of matter at different compositions or states, unrestrained expansion, and friction.

On the other hand, *external* or *exogenous exergy destruction* results from the wastes and emissions that are released into the environment without treatment (Tsatsaronis et al. 2006). Exergy analysis based on only exogenous exergy of the system cannot exclusively justify the efficiency of the system. The sum of internal and external exergy destructions gives the total exergy destruction. Energy analysis cannot quantity the amount of degraded useful work a resource carries thus, the need for exergy analysis which is able to detect locations within the process which may need improvements (Rosen and Dincer 1997).

Mathematically, exergy destruction is defined by Eq. 7.7 and can further be expanded into Eq. 7.8 (Ayres and Ayres 1998; Cornelisse 1997):

$$\sum \mathrm{Ex}_{\mathrm{heat}} - \sum \mathrm{Ex}_{\mathrm{work}} + \sum \mathrm{Ex}_{\mathrm{mass,in}} - \sum \mathrm{Ex}_{\mathrm{mass,out}} = \mathrm{Ex}_{\mathrm{destruction}} = T_0 S_{\mathrm{generation}} = I \tag{7.7}$$

$$\sum \left(1 - \frac{T_0}{T}\right) - W + \left(\sum_i m_i \, \mathrm{Ex}_i\right)_{\mathrm{in}} - \left(\sum_i m_i \, \mathrm{Ex}_i\right)_{\mathrm{out}} = \mathrm{Ex}_{\mathrm{destroyed}} = T_0 S_{\mathrm{generation}} = I \tag{7.8}$$

where $\mathrm{Ex}_{\mathrm{heat}}$, $\mathrm{Ex}_{\mathrm{work}}$, $\mathrm{Ex}_{\mathrm{mass,in}}$ and $\mathrm{Ex}_{\mathrm{mass,out}}$ represent the exergy destruction due to heat, work, mass inputs, and mass outputs, respectively. $\mathrm{Ex}_{\mathrm{destruction}}$, $\mathrm{S}_{\mathrm{generation}}$, m_i and Ex_i represent exergy destruction, entropy generation, mass of resource/stream, and exergy of resource/stream, respectively. W = Work, Ex_i = exergy of *i*th component, m_i = mass of *i*th component, I = irreversibility, T and T_0 are the temperature of the stream/resource, and environmental/reference temperature (298.15 K).

Exergetic efficiency is defined as the ratio of the total exergy flow output to the total exergy flow input and can be expressed mathematically by Eq. 7.9 (Rivero et al. 1999):

$$\mathrm{Ex}_{\mathrm{efficiency}} = \frac{\mathrm{Ex}_{\mathrm{flow-out}}}{\mathrm{Ex}_{\mathrm{flow-in}}} \tag{7.9}$$

The exergy efficiency is a measure of a system's ability to transform raw materials into useful products. For a thermodynamically sustainable system, the exergy efficiency must be nearer to 1 or 100 %. Production systems are considered thermodynamically unsustainable if large amounts of exergy resources are consumed compared to that produced as useful products (Wall 2010). The reduction of exergy losses during a process shifts it to a more exergetic efficient system whereby the conversion performance of the system is improved and the generation of wastes and emissions from the system are reduced.

7.4 Methodology for Exergy Analysis of Biofuels Production from Oil Palm Biomass

In this chapter, the methodology adopted to assess the thermodynamic feasibility of biofuels production from oil palm biomass follows the order:

- System boundary and functional unit definitions.
- Materials and energy flow balance for unit operations within the production systems.
- Chemical exergy calculations for individual streams.
- Physical Exergy calculations for individual streams with the help of Aspen Plus software.
- Exergy balance calculations for each unit operation within the production system.
- Determination of exergy destruction and exergy efficiencies for the production systems.

Almost all the current researches on exergy analysis of biofuels have concentrated only on the units for feedstocks conversion without consideration of the cultivation units. However, this chapter focuses on full exergy analysis of palm biofuels from feedstock extraction to biofuel production. In this chapter, biofuels like biodiesel from crude palm oil (CPO), biodiesel from palm fatty acid distillate (PFAD), bio-oil from empty fruit bunches (EFB), bioethanol from oil palm fronds (OPF), biogas from palm oil mill effluent (POME), and pelletized fuel from oil palm trunks (OPT) are assessed for thermodynamic sustainability.

In this chapter, the production of machinery, equipment, chemicals as well as the construction of all infrastructures like buildings were not included in the system boundary. The reason for these exclusions is that this study did not consider cumulative exergy consumption (CExC) values which considers the production of all the input resources [except the production of palm fresh fruit bunches (FFB)]. Diesel fuels used in transportation are also not included except the use of fuels to convey raw materials, etc., to unit operations within the production plants.

Control of emissions from harvesters and other agricultural machines are not included in the system boundary. They are also considered as part of the waste streams in the plant.

The chemical exergy for each pure substance, organic, and utilities was calculated using their standard chemical exergies ($\mathrm{Ex}^0_{\mathrm{ch},i}$) from the literature (Szargut 1989; Ayres and Ayres 1998; Rivero and Garfias 2006) using Eq. 7.10:

$$\mathrm{Ex}_{\mathrm{ch},i} = \Delta G_f^0 + \sum_i v_i \, \mathrm{Ex}^0_{\mathrm{ch},i} \tag{7.10}$$

where $\mathrm{Ex}_{\mathrm{ch},i}$ = chemical exergy of substance, ΔG_f^0 = standard Gibbs free energy of formation, $\mathrm{Ex}_{\mathrm{ch},i}^0$ = standard chemical exergy of component *i*, v_i = mole ratio of the *i*th component.

The environmental conditions chosen are $T_0 = 298.15$ K and $P_0 = 101.325$ kPa, which are equal to those for thermodynamic standard states, thus the standard chemical exergy is taken to be the same as the chemical exergy of all the species, i.e., $\mathrm{Ex}_{\mathrm{ch},i}^0 = \mathrm{Ex}_{\mathrm{ch},i}$

The standard chemical exergy of complex chemicals that are not listed by Szargut et al. (1988) can be estimated by using the group contribution method (Shieh and Fan 1983) based on information about their molecular structure in determining the absolute entropy and enthalpy of formation values at standard conditions. This method has been used for the exergy calculations of pesticides and packaging materials (Schenk 2001). The Gibbs energy of formation can also be estimated directly for organic compounds, gases, and liquids with the method developed by Krevelen and Chermin (1952). It can also be found using the element method in which the chemical exergy is calculated by using the sum of the products of the stoichiometric coefficients of the elements in the formation reaction and the exergy values of the elements, and the Gibbs energy of formation values at the same standard temperature and pressure (Reid et al. 1977).

The total exergy of utilities such as steam, solar radiation, electricity, etc., were calculated using energy balance results from both production processes. The chemical exergy of steam was calculated using the standard chemical exergies of hydrogen and oxygen for the formation of water. Electricity exergy is taken as 1 MJ which is the same as its power value. Equation 7.11 estimates the exergy of solar radiation (Talens et al. 2010):

$$\mathrm{Ex}_{\mathrm{solar\_radiation}} = \mathrm{Surface\_Area}\,(\mathrm{km}^2) \times \mathrm{Solar\_Radiation}\,(\mathrm{MJ/m}^2\,\mathrm{year}) \times \beta \tag{7.11}$$

β value for biomass (i.e., 1.15) is obtained from the literature (Jørgensen and Svirezhev 2004) for oil palm seedlings and FFB production for 2 years.

Based on the mass and energy balance calculations, the process was simulated to obtain thermodynamic or physical properties of each stream. The physical exergy of each stream is, therefore, calculated using Eq. 7.1.

Since work is considered a pure exergy, the work value given by Aspen Plus can be used directly as the exergy due to work interactions within that stream. A positive work/heat/mass stream sign identifies an entry stream (consumption) while a negative sign of work/heat/mass identify exiting stream (generation) of an equipment within the process. For the purpose of consistency and clear explanation of results, all entering and exiting streams are assigned positive values. Two performance parameters namely exergy destruction and exergy efficiency are determined for all biofuels production systems in this chapter. The exergy destructions are calculated based on both the internal and external exergy destructions described by Rivero et al. (1999).

The internal exergy destruction is calculated by deducting the total exergy output ($\mathrm{Ex_{out}}$) from the total exergy input ($\mathrm{Ex_{in}}$) for every single unit operation as shown by Gouy-Stodola theorem in Eq. 7.12:

$$\mathrm{Ex_{dest-internal}} = \sum \mathrm{Ex_{in}} - \sum \mathrm{Ex_{out}} = T_0 \Delta S \tag{7.12}$$

where $\mathrm{Ex_{dest-internal}}$, $\mathrm{Ex_{in}}$, $\mathrm{Ex_{out}}$, ΔS and T_0 represent internal exergy destruction, exergy of mass flow in, exergy of mass flow out, entropy change ($S - S_0$), and environmental temperature (298.15 K), respectively.

The external exergy destruction is equal to the sum of the exergy of all waste streams in the production process as shown in Eq. 7.13:

$$\mathrm{Ex_{dest-external}} = \sum \mathrm{Ex_{waste-to-environment}} \tag{7.13}$$

where $\mathrm{Ex_{dest-external}}$ and $\mathrm{Ex_{waste-to-environment}}$ represent external exergy destruction and exergy of wastes released into the environment, respectively.

Hence, the total exergy destruction is found by adding the internal and external exergy destructions as shown in Eq. 7.14:

$$\mathrm{Ex_{dest-total}} = \mathrm{Ex_{dest-internal}} + \mathrm{Ex_{dest-external}} \tag{7.14}$$

Aspen Plus software is a process modeling tool for steady-state simulation, design, performance monitoring, optimization, and business planning for chemicals, specialty chemicals, petrochemicals, and metallurgy industries (Aspen Tech 1988). Aspen Plus software (Aspen Tech 2004) has a databank of physical properties for most of the pure, organic, and inorganic substances. Throughout the studies, for systems involving vapor–liquid components such as methanol and glycerol, the NRTL model was used to predict the activity coefficients of the components in the liquid phase (Prausnitz et al. 1980). NRTL model is developed to capture the local concentration gradient between the molecule of interest and the surrounding media. This scenario creates an interaction energy difference among the involved molecules (Prausnitz et al. 1999).

Regardless of the thermodynamic option set used in the simulation of a process with Aspen Plus, enthalpy and entropy values at reference conditions are evaluated Rivero et al. (1999). Physical exergy can therefore be calculated manually using Eq. 7.1 with the thermodynamic results (enthalpy and entropy values) generated by Aspen Plus.

7.4.1 Exergy Analysis of Oil Palm Cultivation

The practices involved in the cultivation of oil palm are discussed in detail in Chap. 3 (Sect. 3.3). In the plantation unit, apart from the FFB obtained as the main product, OPF, OPL, and OPT are considered valuable products which can be transformed into other palm biofuels. OPT is mostly available during replanting of new oil palm seedlings; thus in this study, OPF is considered the significant palm biomass as output resource from the palm cultivation system. Energy contributions from manual harvesting, field maintenance, etc., are converted into energy quantities (MJ) and included in the system boundary. A functional unit of 1 ton palm FFB is chosen. Some assumptions made in this study include:

- 1 ha of oil palm cultivated land produces 35 tons FFB.
- 0.13 kg oil palm seeds produce 0.69 kg oil palm seedlings.
- 1 ton of FFB produced generates 359.0 kg OPF (including OPL).

From normalized published research (Schmidt 2007; Yusoff 2006; Halimah et al. 2012; Nikander 2008) for oil palm nursery and plantation, 1,000 kg FFB requires 0.66 kg of palm seeds with fertilizer and pesticides applications for two years. The nursery is irrigated manually while a pump driven by fossil fuel does the plantation system's irrigation. Harvesting, field establishment, and maintenance are carried out manually with appropriate tools. The direct energy use per hectare of farming land in the whole farming processes are calculated with Eq. 7.15 for mechanized cropping system (Bockari-Gevao et al. 2005):

$$\mathrm{ED} = h \times \mathrm{AFU} \times \mathrm{PEU} \times \mathrm{RU} \tag{7.15}$$

where

h	specific working hours per run (h/ha)
ED	specific direct energy use (fuel) for field operation (MJ/ha)
AFU	average fuel use per working hour (l/h)
PEU	specific energy value per liter of fuel (MJ/l)
RU	runs (number of applications in the considered field operation)

The labor energy input (MJ/ha) at every stage in the production system was estimated by Eq. 7.16 (Bockari-Gevao et al. 2005):

$$\mathrm{LABEN} = \frac{\mathrm{LABOUR} \times \mathrm{TIME}}{\mathrm{AREA}} \times \mathrm{LABENF} \tag{7.16}$$

where

LABEN	labor energy (MJ/ha)
LABOR	number of working laborers
TIME	operating time (h)
AREA	operating area (ha)
LABENF	labor energy factor (MJ/h).

Oil palm cultivation system was not in complete material balance due to the continuous farming which may last for years. Since the structure of oil palm biomass is not well-defined, the thermodynamic properties are not exactly known. For instance, assuming the composition of the biomass to be $C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}S_{\varepsilon}$, then based on the biomass combustion heat of reaction, the enthalpy change of formation, ΔH_f^0

value of the biomass can be calculated where α, β, γ, δ, and ε are the mole contents of the elements C, H, O, N, and S, respectively, obtained from the ultimate analysis of the biomass (Jørgensen and Svirezhev 2004). Figure 7.1 summarizes the materials, energy, and exergy balances for oil palm cultivation system.

For about 59,573 MJ exergy of materials that entered the FFB cultivation system, about 48,424 MJ came out as exergy of the main products. This implies that about 11,145 MJ of exergy was destroyed for the production of 1 ton FFB. The overall exergy efficiency of the cultivation system is about 81.3 % with about 0.74 % being the exergy of wastes (polythene bags used for nursery). However, the nursery unit recorded about 34 % exergy efficiency with about 315 MJ exergy destroyed. Though the exergy destroyed in the FFB production system was higher (10,750 MJ) than that for the nursery system, it was more exergetically efficient. The main products from the nursery unit were oil palm seedlings and polyethene bags (wastes) which had low exergy contents compared to those of the input resources. This scenario always renders a system exergetically inefficient. In the FFB production unit, FFB and OPF were the main products whose exergy contents were high and closer to those of the inputs hence small amount of exergy destroyed. The exergy content of the main input into the cultivation system (i.e., oil palm seeds) was upgraded from 13.8 to 40,463 MJ (for FFB). The cultivation of 1 ton of FFB can be considered exergetically efficient since its efficiency is near 1 (0.81). Scaling up of this system may reduce the exergy destruction drastically as large quantities of FFB with high exergy contents would be generated as the main product. Another reason for increased exergy destruction in the cultivation system is the dissipative effects of the light source (solar radiation) and the use of fossil fuel which eventually contributed to entropy generation hence exergy destruction in the cultivation unit. Exergy destruction can be minimized though the conversion of wastes into value-added bioproducts. Again, the amounts of input resources like fertilizers, pesticides, etc., could be reduced as they also contain high exergy content.

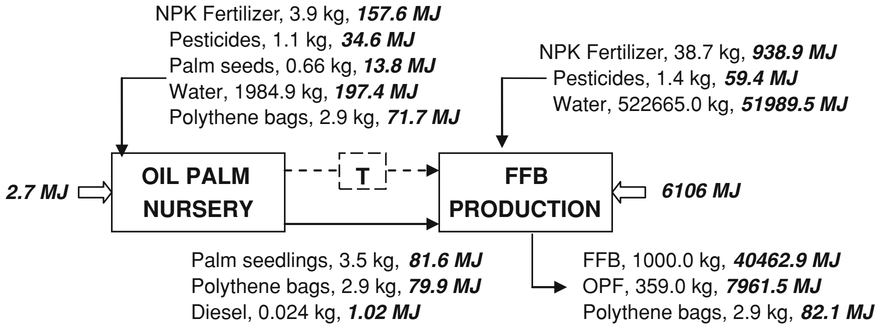
NPK Fertilizer, 3.9 kg, 157.6 MJ
Pesticides, 1.1 kg, 34.6 MJ
Palm seeds, 0.66 kg, 13.8 MJ
Water, 1984.9 kg, 197.4 MJ
Polythene bags, 2.9 kg, 71.7 MJ
NPK Fertilizer, 38.7 kg, 938.9 MJ
Pesticides, 1.4 kg, 59.4 MJ
Water, 522665.0 kg, 51989.5 MJ
2.7 MJ
OIL PALM NURSERY
T
FFB PRODUCTION
6106 MJ
Palm seedlings, 3.5 kg, 81.6 MJ
Polythene bags, 2.9 kg, 79.9 MJ
Diesel, 0.024 kg, 1.02 MJ
FFB, 1000.0 kg, 40462.9 MJ
OPF, 359.0 kg, 7961.5 MJ
Polythene bags, 2.9 kg, 82.1 MJ

Fig. 7.1 Exergy balance for oil palm cultivation

7.4.2 Exergy Analysis of Palm Oil Milling Processes

Chapter 4 (Sect. 4.2.2) discusses the details of the main operations involved in the extraction of CPO from FFB. For 1 ton of FFB processed, about 140, 139.5, and 104 kg of steam are used by the sterilizer, stripper, and digger, respectively. A functional unit of 1 ton CPO is chosen for this section, thus 4,436 kg of FFB is processed to produce 1,145 kg of EFB, 763 kg of PPF, and 695 kg of palm kernel nuts (PKN). The standard chemical exergies for the input and output resources for the palm oil milling unit are shown in Table 7.2. The chemical exergies of FFB, EFB, PKN, PPF, CPO, and all wastes were calculated based on their chemical compositions. Process conditions were obtained from published reports (Ofori-Boateng et al. 2012a; Jaimes et al. 2010). Figure 7.2 summarizes the exergy balance for the production of 1 ton CPO from FFB.

Of about 189,374 MJ exergy of resources that entered the plant, only about 110,647 MJ was available to perform work. This implies that for a production of 1 ton CPO, about 78,727 MJ of exergy is destroyed (internal exergy destruction) representing about 41.6 % of the total exergy of resources that entered the plant as inputs. In the CPO milling unit, about 822 MJ of exergy was generated as wastes (external exergy destruction) representing about 0.43 % of the input exergy. Thus, the total exergy destroyed during the production of 1 ton CPO is about 79,549 MJ. The overall exergy efficiency of the CPO milling unit was about 58.4 %. The exergy of FFB (187,692 MJ) that entered the mill for 1 ton CPO production was drastically reduced to about 110,647 MJ useful product that could produce work. This means that FFB was degraded (i.e., about 59 % of FFB exergy was destroyed) in course of the processes to obtain CPO, PPF, EFB, and PKN. In this study, EFB, PPF, and PKN that were generated as co-products were considered useful products. However, in a circumstance where they are regarded as wastes, the exergy destruction would be as high as 151,386 MJ representing about 80 % of the total exergy content of input resources. This situation would have reduced the exergy efficiency of the whole system to about 20 % (main contribution from external exergy destruction). Thus, the conversion of oil palm biomass like EFB, PPF, and PKN would improve the thermodynamic sustainability of the mill. In most palm oil mills, parts of the PPF and palm kernel shells (PKS) are utilized as boiler fuels for steam and bioelectricity production. EFB presently do not have any commercial use but are rarely digested together with POME to produce biogas of which the slurry is used as biofertilizer in the plantation. However, considering the unit operations individually, the purification and drying of CPO to remove excess water was the most exergetically efficient at 98.6 % with little internal exergy destruction of about 556 MJ. This means that only about 1.4 % of the total exergy inputs were destroyed to obtain CPO from this unit. Water, with very small exergy content (0.049 MJ/kg) was the main component in the entering steam of the purifier/dryer, which needed to be removed. The entering exergy was almost the same as the exiting exergy due to the insignificant exergy content of water hence low internal exergy destruction.

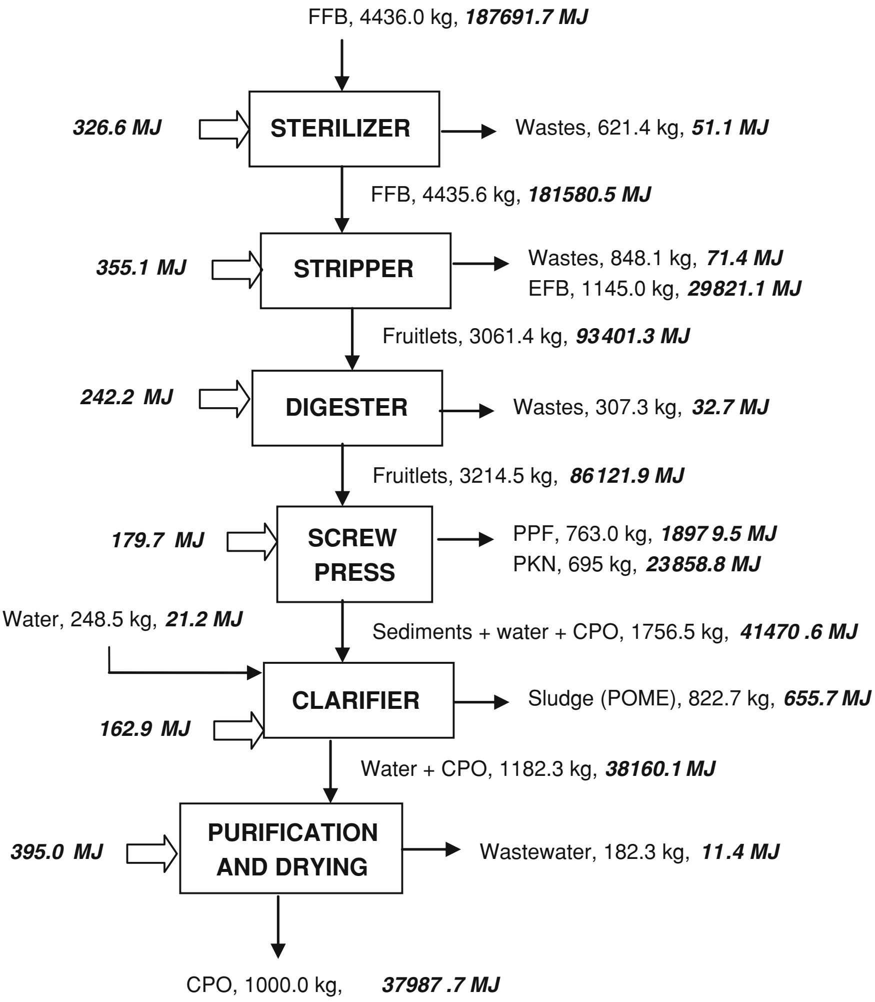
FFB, 4436.0 kg, 187691.7 MJ
326.6 MJ
STERILIZER
Wastes, 621.4 kg, 51.1 MJ
FFB, 4435.6 kg, 181580.5 MJ
355.1 MJ
STRIPPER
Wastes, 848.1 kg, 71.4 MJ
EFB, 1145.0 kg, 29821.1 MJ
Fruitlets, 3061.4 kg, 93401.3 MJ
242.2 MJ
DIGESTER
Wastes, 307.3 kg, 32.7 MJ
Fruitlets, 3214.5 kg, 86121.9 MJ
179.7 MJ
SCREW PRESS
PPF, 763.0 kg, 18979.5 MJ
PKN, 695 kg, 23858.8 MJ
Water, 248.5 kg, 21.2 MJ
Sediments + water + CPO, 1756.5 kg, 41470.6 MJ
CLARIFIER
Sludge (POME), 822.7 kg, 655.7 MJ
162.9 MJ
Water + CPO, 1182.3 kg, 38160.1 MJ
395.0 MJ
PURIFICATION AND DRYING
Wastewater, 182.3 kg, 11.4 MJ
CPO, 1000.0 kg, 37987.7 MJ

Fig. 7.2 Exergy balance for crude palm oil milling processes

The stripper recorded the highest exergy destruction of about 58,642 MJ which was about 32 % of the total exergy inputs. The stripper used high amounts of exergy from fossil fuels which could have increased entropy generation resulting from dissipative effects from fossil fuel use. Again, input exergy from FFB was high and it eventually reduced after the stripping process as seen from Fig. 7.2. If renewable energy is used during the process, it could increase the exergetic efficiency of the stripper. The exergy of wastes from the stripper is not high to affect the exergy efficiency significantly. However, it could be treated and recycled to be used in other unit operations (for instance in the clarifier where water is used) for improved processes in terms of exergy.

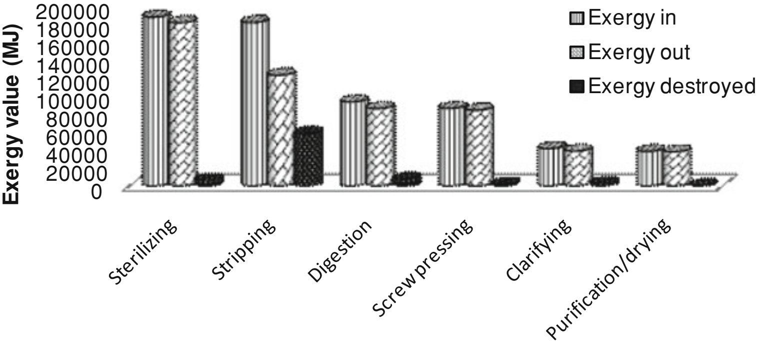

Fig. 7.3 Exergy balance of 1 ton CPO production system

The sterilizer, digester, screw press, and clarifier recorded exergy efficiencies of about 96.6, 92.0, 97.7, and 93.2 %, respectively. These unit operations were highly exergetically efficient though fossil fuels were utilized in the processes. However, the entering resources contained higher exergy than the outputs while the exergy of wastes was also insignificant. The individual subsystems can be considered thermodynamically efficient but the intermediate products like fruitlets which possibly rendered them efficient are not useful unless they are processed into CPO. Thus for the whole milling process, FFB conversion into CPO was not thermodynamically efficient neglecting all the intermediate products. The system could be improved thermodynamically by treating all wastes for recycling within the plant as well as utilizing some co-products for energy production to be utilized by the unit operations. Figure 7.3 shows the distribution of exergy in the unit operations within the palm oil mill.

7.4.3 Exergy Analysis of Biodiesel Production from Crude Palm Oil

CPO, according to this work, is assumed to largely contain the triglycerides C16:0 (palmitic acid, 38.5 %), C18:1 (oleic acid, 37.0 %), C18:3 (Linoleic acid, 8.0 %), and C18:0 (Stearic acid, 4.5 %). In the biodiesel production unit, esterification of CPO with methanol and phosphoric acid (H_3PO_4) is first carried out in a reactor in order to remove the free fatty acid (FFA) from the oil before transesterification. The CPO is then purified in which methanol is recovered simultaneously. In the methanol recovery unit, a ten-ideal stage with total condenser, kettle reboiler, and a 2.5 reflux ratio were used to remove approximately 99 % of the methanol in the CPO stream. Eight ideal stages with total condenser, kettle reboiler, and a 1.5 reflux ratio were used to separate the biodiesel from excess water. It was reported

Table 7.1 Chemical exergy calculations for crude palm oil (CPO)

Component	Standard chemical exergy (MJ/kg)	Mass (kg)	Chemical exergy (MJ)
Triglycerides	38.01	792.15	30,109.62
Free fatty acid	32.22	188.81	6,063.16
Water	0.049	8.55	0.42
Organic matter	16.65	5.49	91.41
Total exergy			36,264.61

Chemical exergy data obtained from Talens et al. (2010)

by Gómez-Castro et al. (2010) that column ideal stage between 9 and 15 is recommended for separation of water and methanol in biodiesel production.

Base-catalyzed transesterification with sodium hydroxide (NaOH) is carried out to convert the CPO into biodiesel and glycerol. The optimum reaction temperature used was 70 °C at 1 bar. About 96.7 % of the triglycerides that enters the transesterification reactor was assumed to be transformed into biodiesel in this study. The methyl ester phase containing glycerides, methyl esters (biodiesel), and methanol was then fed into a water washer at 50 °C in order to purify the biodiesel. Process conditions for this study were chosen based on pilot production data (Choo et al. 2011) and published research data (de Almeida et al. 2002; Ofori-Boateng et al. 2012b, c). A functional unit of 1 ton biodiesel is chosen for this study.

Chemical exergy is calculated using the total mass and chemical composition of the substance of interest together with the specific or standard chemical exergy which is obtained from Szargut et al. (1988). Table 7.1 shows a sample chemical exergy calculations for CPO

Table 7.2 shows the standard chemical exergies for the major input and output resources for the production of biodiesel from CPO. Figure 7.4 shows the exergy balance for biodiesel production from CPO.

Therefore for a kilogram of crude palm oil, $\mathrm{Ex}_{\mathrm{ch},i}^{0}$ (CPO) = 36,264.61/1,000 = 36.26 MJ/kg

In order to produce 1 ton of biodiesel from CPO, about 995 kg of CPO was charged into the biodiesel production unit consisting of esterification and transesterification reactors as well as separation and purification units. CPO was degraded in terms of exergy during the process to form biodiesel. For about 39,524 MJ exergy of CPO that entered the biodiesel production system, about 3,004 MJ exergy was destroyed in order to obtain the palm biodiesel with exergy content of 36,520 MJ. For the whole production system, of the total exergy of input resources of about 52,266 MJ, about 48,725 MJ came out as useful products including biodiesel, recovered methanol, and water. The overall exergy destruction recorded was about 3,539 MJ for 1 ton of palm biodiesel produced. The exergy efficiency of the biodiesel production system was about 93.2 %. Figure 7.5 shows the exergy destruction contributions by the unit operations within the biodiesel production system.

All the production subunits recorded high exergy efficiencies above 97 % with the washer having the highest at about 99.6 %. The CPO purification unit recorded

Table 7.2 Standard chemical exergy values of materials used in oil palm cultivation, palm oil milling, and biodiesel production

Substance	Standard chemical exergy ($Ex^0_{ch,\ i}$) (MJ/kg)
Biodiesel	35.55
Crude palm oil (CPO)	36.26
Diesel fuel	42.70
Electricity	1.00
Empty fruit bunches (EFB)	18.50
Fresh fruit bunches (FFB)	40.21
Glycerol	22.30
Methanol	22.44
NPK Fertilizer	18.57
Oil palm fronds (OPF)	19.93
Oil palm seeds	17.71
Oil palm seedlings	18.09
Oil palm trunks (OPT)	20.11
Palm kernel nuts (PKN)	31.45
Palm pressed fiber (PPF)	17.77
Pesticides	19.13
Phosphoric acid (H_3PO_4)	0.914
Polythene bags	18.57
Sodium hydroxide (NaOH)	1.873
Solar energy	0.04595
Steam	0.526
Water	0.049

Source Rivero and Garfias (2006), Szargut et al. (1988), Ofori-Boateng et al. (2012c), Ojeda et al. (2011)

the lowest exergy efficiency of about 97.4 % and contributed about 34 % of the total exergy destruction for the whole plant. The total useful energy destroyed in the biodiesel production unit was about 3,447 MJ (exergy efficiency of 93.2 %) which is closer to the reports from other researches, which utilized different feedstocks. Jaimes et al. (2010) has also reported that about 42 % of the total exergy destruction for the biodiesel production system was contributed by the purification and separation systems. Ofori-Boateng et al. (2012a, b, c) reported a total exergy destruction of about 1,262 MJ (exergy efficiency of 83 %) and 1,275 MJ (exergy efficiency of 92 %) for the conversion of microalgal and *Jatropha curcas* oil into biodiesel, respectively, considering 1 ton of biodiesel produced. The conversion of microalgal oil into biodiesel has again been assessed by Peralta et al. (2010) and Sorguven and Ozilgen (2010) to have exergy destructions of about 7,232 MJ (79 % exergy efficiency) and 190 MJ (70 % exergy efficiency), respectively, for 1 ton biodiesel produced. Talens et al. (2010) calculated the exergy efficiency of a production system for 1 ton biodiesel from used cooking oil to be as high as 98 % with the assumption that all waste streams are utilized. Comparing these reports with the results of this study, palm biodiesel is considered more exergetically efficient than microalgal and jatropha biodiesel

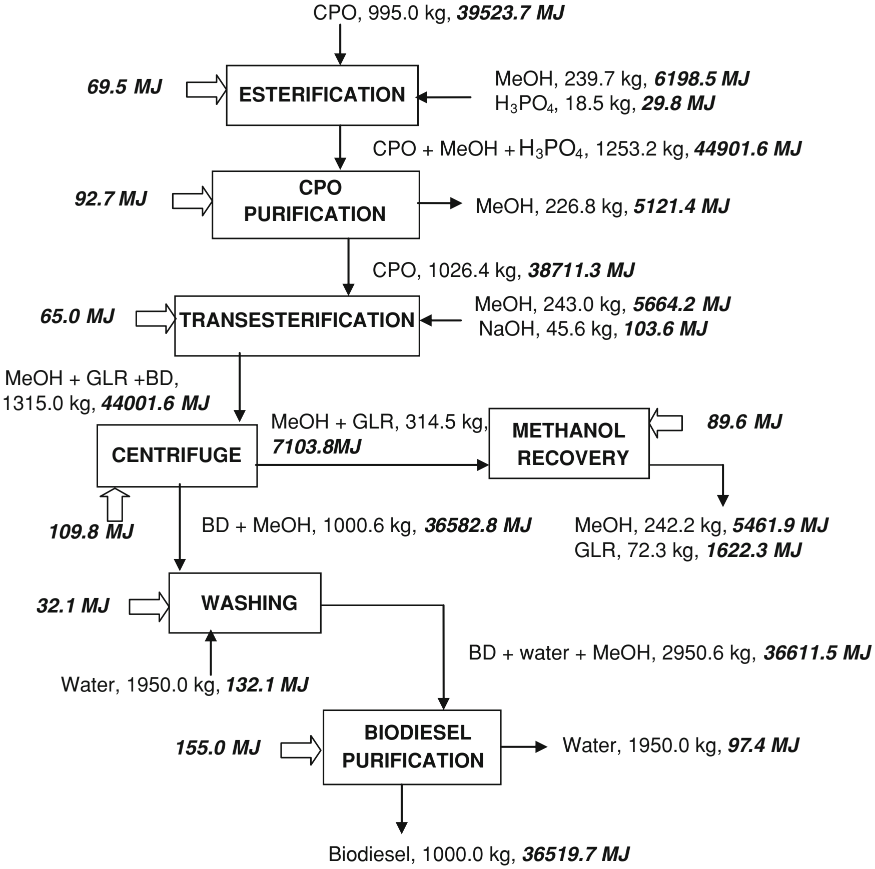
CPO, 995.0 kg, **39523.7 MJ**
69.5 MJ
ESTERIFICATION
MeOH, 239.7 kg, **6198.5 MJ**
H_3PO_4, 18.5 kg, **29.8 MJ**
CPO + MeOH + H_3PO_4, 1253.2 kg, **44901.6 MJ**
92.7 MJ
CPO PURIFICATION
MeOH, 226.8 kg, **5121.4 MJ**
CPO, 1026.4 kg, **38711.3 MJ**
65.0 MJ
TRANSESTERIFICATION
MeOH, 243.0 kg, **5664.2 MJ**
NaOH, 45.6 kg, **103.6 MJ**
MeOH + GLR +BD, 1315.0 kg, **44001.6 MJ**
CENTRIFUGE
MeOH + GLR, 314.5 kg, **7103.8MJ**
METHANOL RECOVERY
89.6 MJ
109.8 MJ
BD + MeOH, 1000.6 kg, **36582.8 MJ**
MeOH, 242.2 kg, **5461.9 MJ**
GLR, 72.3 kg, **1622.3 MJ**
32.1 MJ
WASHING
Water, 1950.0 kg, **132.1 MJ**
BD + water + MeOH, 2950.6 kg, **36611.5 MJ**
155.0 MJ
BIODIESEL PURIFICATION
Water, 1950.0 kg, **97.4 MJ**
Biodiesel, 1000.0 kg, **36519.7 MJ**

Fig. 7.4 Exergy balance for biodiesel production from CPO

production systems when all waste streams like wastewater, glycerol, etc., are utilized for value-added bioproducts.

Energy integration as well as efficient equipment design could reduce these destructions in order to make the system more thermodynamically sustainable. Again, separation parameters like retention time must be carefully chosen and monitored in order to ensure efficient operations by the separation equipment.

This study assumed the treatment and possible utilization of all wastes generated from each of the unit operations. Methanol was recovered for reuse while wastewater from the separation units was considered to be treated before discharge. With all these assumptions not made, the system would have recorded much higher exergy destruction which would eventually reduce the exergy efficiency.

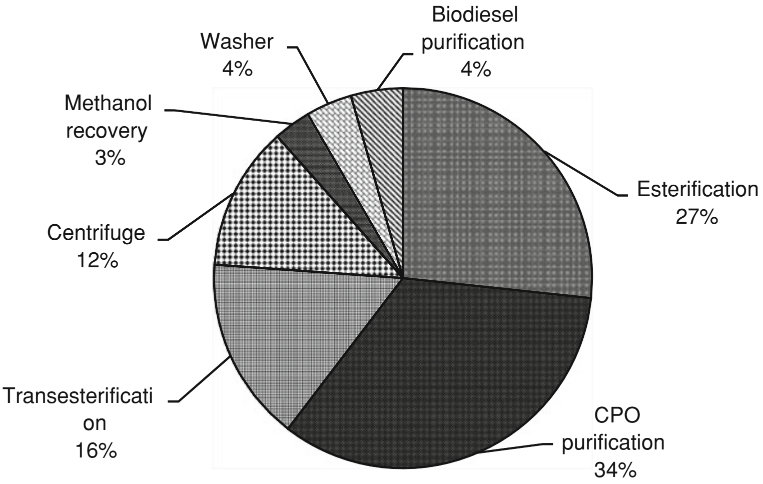

Fig. 7.5 Exergy destruction contributions by unit operations in the biodiesel production system

7.4.4 Exergy Analysis of Bioethanol Production from Oil Palm Fronds (OPF)

The data used in this study were obtained from published research reports (Goh et al. 2012; Ojeda and Kafarov 2009; Hamelinck et al. 2005; Ofori-Boateng and Lee 2013).

Separate hydrolysis and fermentation of OPF is chosen as case study for this section and this method involves three major processes namely pretreatment, hydrolysis (or saccharification), and fermentation. Bioethanol production from lignocellulosic materials like OPF requires the removal of lignin and other extractives in order to expose the holocellulose and increase cellulose crystallinity for easy enzyme or acid catalyst activities. The pretreatment stage is vital to facilitate the production of sugars from the cellulosic material as it has been found that bioethanol production from nonpretreated biomass generated less than 20 % sugar yield as against over 90 % yield for pretreated biomass (Hamelinck et al. 2005).

During the pretreatment process, the OPF obtained from the oil palm plantation were washed, cut into smaller pieces, dried, and milled in order to increase its surface area for maximum chemical/enzyme penetration. The pretreatment stage is found to be one of the energy intensive stages for the production of sugars from lignocellulosic materials (Ojeda and Kafarov 2009). Again, the pretreatment stage for cellulosic ethanol generates large quantities of utilizable wastes that are not tapped for value-added bioproducts. Thus there must be the need to assess its exergetic efficiency in order to improve the process for sustainable bioethanol production. Some cost effective ways of pretreating lignocellulosic materials for bioethanol production include the applications of steam explosion or hot water, dilute acid/alkaline, lime, ammonia, etc. (Moiser et al. 2005). In this study, steam explosion is chosen as a pretreatment method. The pretreated OPF then undergo acid hydrolysis and fermentation separately.

Hydrolysis is a chemical reaction which converts complex polysaccharides (e.g., starch, cellulose, chitin, glycogen, etc.) in biomass into simple sugars (i.e., monosaccharides) such as glucose (dextrose), galactose, fructose, hexose, xylose, ribose, etc., which is commonly catalyzed by enzymes, acids, and alkaline. Saccharification of the prehydrolysate with dilute sulfuric acid (H_2SO_4) for the conversion of the cellulose into sugars is used in this study. H_2SO_4 is preferred as catalyst for acid hydrolysis because it remains in the hydrolysate (after neutralization with NaOH) as nutrients for microorganisms during fermentation and eventually improves the economics of the process (Gámez et al. 2006). The separation process is therefore eliminated hence, reduction in 'energy' use. Glucose yield of about 70–85 % (compared to about 95–99 % for enzymatic hydrolysis) is achieved with acid hydrolysis due to the production of furfural (Gámez et al. 2006). In this study, about 5 wt% acid concentration is used for the hydrolysis of steam exploded OPF. The hydrolysate then enters the fermentation reactor where the sugars are converted into bioethanol.

Fermentation is a biochemical reaction which converts the simple sugars from the hydrolysis reaction into bioethanol (with carbon dioxide as by-product) with the help of yeast (mostly *Saccharomyces cerevisiae*). In this work, fermentation of the sugars was aided by baker's yeast (*S. cerevisiae*). The resulting bioethanol which contains water and impurities is separated by stripping and dehydration using molecular sieves.

The fresh OPF chemical compositions include 20.5 % lignin, 49.8 % cellulose, 33.7 % hemicellulose, 2.4 % ash, and 4.5 % extractives (Wan Zahari et al. 2004). After pretreatment, the considered compositions of the OPF prehydrolysate for simulation are 16.53 % lignin, 38.52 % cellulose, and 30.95 % hemicellulose (Goh et al. 2012).

A functional unit of 1 ton bioethanol is chosen for the exergy analysis in this study. In order to produce 1 ton of bioethanol, 3 tons of OPF is used as the feed mass. All wastes within the bioethanol production system are considered untreated. The production of input resources as well as the utilization of lignin (as by-product) is not part of the system boundary. Steady-state reaction conditions as well as the NRTL model for the calculation of the activity coefficients for the components due to the presence of liquid–vapor phases (Prausnitz et al. 1980). Hexose sugars were represented by glucose while pentose sugars were also represented by xylose. Table 7.3 summarizes the production conditions used for the mathematical modeling with Aspen Plus software.

Chemical exergy is calculated using the total mass and chemical composition of the substance of interest together with the specific or standard chemical exergy which is obtained from Szargut et al. (1988). For instance, the specific chemical exergy of OPF is found from the correlation by Eq. 7.16 (Szargut et al. 1988):

Table 7.3 Production conditions for bioethanol production from OPF

Production stage	Production conditions	Sugar yield (%)	
		Glucose	Xylose
Pretreatment	Steam explosion, 160 °C, 1 atm		
Saccharification (hydrolysis)	Dilute H_3PO_4, 2.5 % w/v, 175 °C, 3.5 atm	35.8	67.8
Fermentation	Yeast (*Saccharomyces cerevisiae*), 20 FPU/g, 303 K, 1 atm		

Sources Millati et al. (2002), Palmqvist and Hahn-Hagerdal (2000), Goh et al. (2012)

$$\begin{aligned}\mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{OPF}) = {} & \left[0.498 \times \mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{cellulose})\right] + \left[0.337 \times \mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{hemicellulose})\right] \\ & + \left[0.205 \times \mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{lignin})\right] + \left[0.024 \times \mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{Ash})\right] \\ & + \left[0.045 \times \mathrm{Ex}^0_{\mathrm{ch},i}(\mathrm{Extractives})\right]\end{aligned} \tag{7.16}$$

The standard chemical exergy values for the major compounds used in this study are shown in Table 7.2 with references from Szargut et al. (1988). For other compounds whose standard chemical exergy values are not found in the literature, a similar correlation in Eq. 7.16 is used to compute them. For chemical exergies of utilities involved with electricity, 1 MJ of electrical energy was assumed to correspond to an exergy flow of 1 MJ (Talens et al. 2007).

Physical exergy of each stream was found with the help of Aspen Plus software version 2006 after simulation and other values from Wooley and Putsche (1996). The enthalpy and entropy values generated from the software were used with the help of Eq. 7.3 to calculate for the physical exergies. Total exergies were then found for each stream and the calculations for exergy destructions (both internal and external) for every unit operation within the production system were calculated accordingly. Table 7.4 shows the standard chemical exergy contents of input and output resources for the production of bioethanol from OPF. Figure 7.6 summarizes the exergy balance estimation for the OPF bioethanol production.

Considering the whole bioethanol production system, about 36,815 MJ of 'quality energy' was destroyed for every ton of bioethanol produced from OPF. The exergy efficiency of the system was 52.5 % when it was assumed that the lignin could be used in the combined heat and power generation plant in the palm oil mills while wastewater could be treated and recycled for use in the bioethanol production system. Of about 69,812 MJ of useful energy in OPF that underwent the processing, about 37.1 % was destroyed in order to obtain the final product, bioethanol. The exergy efficiency would be lower if lignin and waste streams are not utilized for value-added bioproducts.

The feed preparation subsystem consisted of washing, milling, and drying units. For a production of 1 ton bioethanol from OPF, this subsystem contributed about 23.5 % of the total exergy destroyed. However, the feed preparation unit had an

Table 7.4 Standard chemical exergy values of materials used in palm bioethanol production from OPF

Substance	Standard chemical exergy ($Ex^0_{ch,i}$) (MJ/kg)
Acetic acid	4.94
Ash	0.202
Bioethanol	24.55
Carbon dioxide (CO_2)	0.443
Cellulose	12.52
Diesel fuel	42.70
Electricity	1.00
Extractives (mainly phenolic compounds)	14.23
Furfural	11.31
Glucose	12.72
Hemicellulose	9.12
Lactic acid	8.44
Lignin	18.79
Oil palm fronds (OPF)	19.93
Sodium hydroxide (NaOH)	1.873
Sulfuric acid (H_2SO_4)	1.66
Steam	0.526
Water	0.049
Xylose	10.02
Yeast	7.93

Source Rivero and Garfias (2006), Ofori-Boateng et al. (2012a), Ojeda et al. (2011)

exergy efficiency of 88.5 %. The total exergy of wastes from this unit was 779.9 MJ which resulted from the discharge of wastewater used in the washing of OPF before drying and milling. If the wastewater is not treated and recycled, the overall exergy efficiency would reduce. Fossil fuel use in drying and other unit processing contribute to emissions into the environment hence reduction in the efficiency of the system thus fossil fuel use must be minimized.

Steam explosion subsystem which consisted of steam explosion tank and drying unit contributed the highest exergy destruction of about 59.3 % for the whole bioethanol production. About 69.9 % exergy efficiency was recorded for the steam explosion of OPF for 1 ton bioethanol production. Most of the valuable energy available within the input resources (mainly OPF with total exergy of 61,778 MJ) to perform work was degraded (to an exergy content of 41,333 MJ) due to entropy generation within the system leading to irreversibilities. The efficient design of the steam explosion reactor as well as suitable operation conditions would help reduce some of these inefficiencies in exergy contents of materials that come out as products from the reactor.

The hydrolysis rector also recorded the next highest exergy destruction after steam explosion unit. The overall exergy efficiency for the hydrolysis reactor was about 72.8 %. The chemical and thermal processes that occurred in the hydrolysis reactor contributed to entropy generation, hence exergy destruction. Minimization

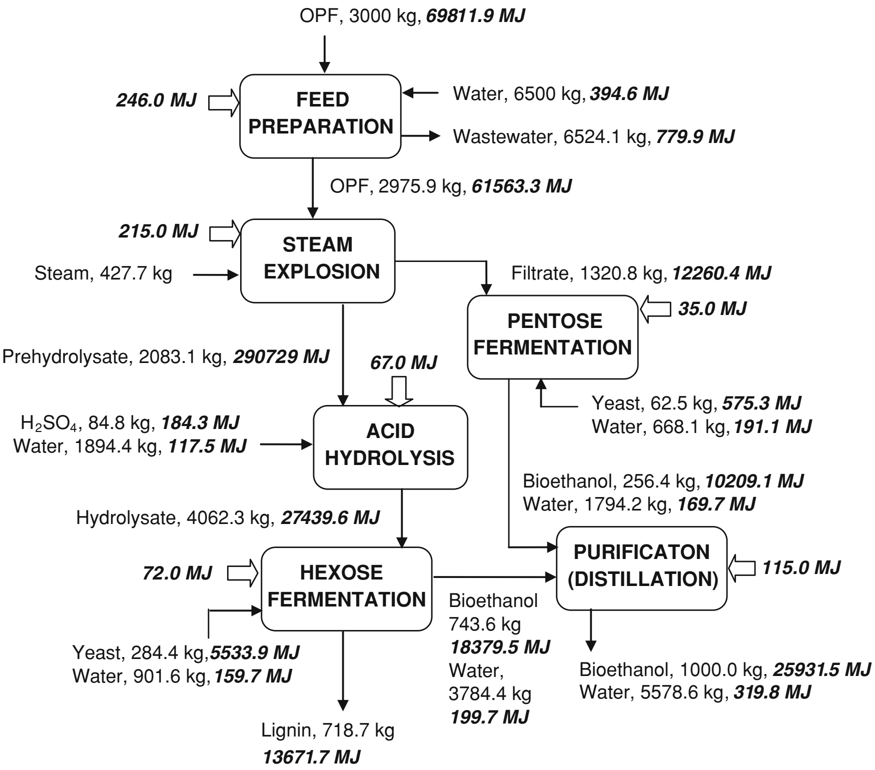
OPF, 3000 kg, **69811.9 MJ**
246.0 MJ
FEED PREPARATION
Water, 6500 kg, **394.6 MJ**
Wastewater, 6524.1 kg, **779.9 MJ**
OPF, 2975.9 kg, **61563.3 MJ**
215.0 MJ
Steam, 427.7 kg
STEAM EXPLOSION
Filtrate, 1320.8 kg, **12260.4 MJ**
PENTOSE FERMENTATION
35.0 MJ
Prehydrolysate, 2083.1 kg, **290729 MJ**
67.0 MJ
Yeast, 62.5 kg, **575.3 MJ**
Water, 668.1 kg, **191.1 MJ**
H_2SO_4, 84.8 kg, **184.3 MJ**
Water, 1894.4 kg, **117.5 MJ**
ACID HYDROLYSIS
Bioethanol, 256.4 kg, **10209.1 MJ**
Water, 1794.2 kg, **169.7 MJ**
Hydrolysate, 4062.3 kg, **27439.6 MJ**
72.0 MJ
HEXOSE FERMENTATION
PURIFICATON (DISTILLATION)
115.0 MJ
Bioethanol 743.6 kg **18379.5 MJ**
Water, 3784.4 kg **199.7 MJ**
Yeast, 284.4 kg, **5533.9 MJ**
Water, 901.6 kg, **159.7 MJ**
Bioethanol, 1000.0 kg, **25931.5 MJ**
Water, 5578.6 kg, **319.8 MJ**
Lignin, 718.7 kg **13671.7 MJ**

Fig. 7.6 Exergy balance for bioethanol production from OPF

of chemical use or their replacement with enzymes could help reduce the exergy destruction though enzymes are costly.

The fermenters (xylose and glucose fermentation reactors) also recorded some amount of irreversibilities due to the inhibition effect of glucose and xylose accumulations within the reactors (Ojeda and Kafarov 2009). The enzyme velocity is therefore reduced at low substrate concentration, hence causing the reduction in exergy efficiencies. The exergy efficiency of the pentose fermenter (88.5 %) was lower than that of the hexose fermenter (97.1 %) due to process inefficiencies leading to high exergy destruction in the pentose fermenter. The pentose and hexose fermenters contributed about 7.8 and 2.8 % to the total exergy destroyed in the bioethanol production system.

On the other hand, the purification unit recorded about 282.7 MJ of exergy destruction, which is about 0.82 % of the total exergy destroyed by the bioethanol production system. The overall exergy efficiency of the bioethanol purification unit was about 90.3 %. In this unit, entropy generation was minimal perhaps due to efficient process and equipment design. The process conditions were favorable which contributed to minimal destruction of exergy of the bioethanol.

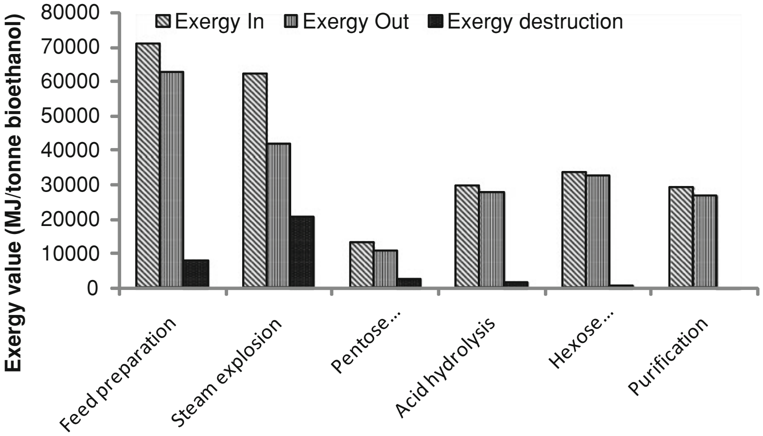

Fig. 7.7 Exergy destruction contributions by unit operations in bioethanol production system

The exergy content of OPF was, however, degraded from 69,812 to 25,932 MJ with about 37.1 % useful exergy destroyed in the OPF. The bioethanol could gain high exergy content when the whole production process is improved through process and equipment design as well as utilization of wastes for value-added bioproducts (Ofori-Boateng and Lee 2013). Figure 7.7 shows the contributions of exergy destruction by the unit operations within the bioethanol production system for 1 ton bioethanol production from OPF.

7.4.5 Exergy Analysis of an Integrated System for Biomethane and Bioelectricity Production from POME

The system boundary for the integrated biogas and bioelectricity production from POME used for the exergy analysis in this section did not include the production of all raw materials, equipment, and buildings. The digestate generated after anaerobic digestion was considered as a useful material that can be used in the oil palm plantation as biofertilizer.

In a typical palm oil mill where POME is treated in open ponds, the POME generated from processing 1 ton of FFB/h is able to produce about 333 m^3 biogas which comprises about 64 % methane, 35 % CO_2, and traces of hydrogen sulfide and water vapor (Ma 1999). This amount of POME can produce about 115 MJ electricity to add to the bioenergy used in the mill.

Joanta (1996) estimated a total of about 1.04 MW bioenergy that could be generated from about 12,000 m^3 of biogas produced per day from POME obtained from the processing of about 60 tons of FFB/h. In Malaysia, there exist over 400 palm oil mills with a total installed CHP capacity of about 261.1 MW, which are capable of generating over 1.88 MW/h of bioelectricity (NKEA, 2011).

In this study, it is assumed that POME generated from the palm oil mill is directly charged into the homogenizer where mixing is done to enhance microbes activities for high biogas yield. POME contains about 95 % water, 4 % residual oil (FFA content of 30–70 %), and 1 % sediments. About 1 m^3 of POME, which is equivalent to 1,500 kg, can generate about 28 m^3 of biogas and a m^3 of the biogas produced can generate about 0.3453 MJ bioelectricity. About 97 % of the POME after anaerobic digestion remains as the digestate which can be used as biofertilizer (Sežun et al. 2010).

The homogenized POME then enters the anaerobic digester for fermentation to occur. About 80–90 % of palm oil mills in Malaysia use the anaerobic and facultative ponding systems for treating POME because they are relatively cheap (Ma and Ong 1985). However, there are some commercial palm oil mills that treat their POME using closed-tank anaerobic bioreactors for biogas capture (Quah 1987) though they require long residence time. Exergy analysis is carried out on a close-tanks anaerobic digester which operates at mesophilic temperature (37 °C) (Yejian et al. 2011). For a kilogram of POME processed, about 0.23 MJ of energy (both electrical and heat) is needed by the anaerobic digester to produce the biogas (Berglund and Börjesson 2006; Börjesson and Berglund (2007)).

The biogas produced from the anaerobic digester is a mixture of CH_4, CO_2, H_2S, and traces of water vapor. In order to upgrade the biomethane as the main product for bioelectricity production, a scrubbing unit is employed and the CO_2, H_2S, and water vapor are trapped by a gas stack while the biomethane goes into the CHP plant for electricity generation. What most palm oil mills do is to capture their biogas, and flare or release them into the atmosphere causing environmental burdens (Lantz et al. 2007). The biogas purification unit also requires about 0.0018 MJ of energy to process 1 kg of biogas (Murphy and McCarthy 2005) before being fed into the gas turbine for bioelectricity generation. Energy use within the biogas plant is assumed to be sourced from fossil fuel. Water consumption for the removal of impurities from the biogas is assumed to be 1 kg for every cubic meter of biomethane generated (Benjaminsson et al. 2010).

Biomethane then enters the CHP plant for bioelectricity generation. The CHP plant consists of compressors and gas turbines, which have pistons within which the biomethane is combusted. The energy resulting from the biomethane combustion is used to rotate a shaft which converts chemical energy in the biomethane into mechanical energy. This energy then powers an alternating current shaft, which eventually produces the electricity through magnetism. A functional unit of 1 MJ bioelectricity is chosen for this study.

Table 7.5 shows the standard chemical exergies of the main input and output resources for bioethanol production from OPF. Data used for the materials and energy balance calculations were obtained from published research reports (Yejian et al. 2011; O-Thong et al. 2012; Hosseini and Abdul Wahid 2013). Figure 7.8 summarizes the exergy balance calculations for the production of biomethane and bioelectricity from POME.

The main inputs into the biomethane and bioelectricity generation systems were POME, heat, and steam. The total exergy of these input resources was about

Table 7.5 Standard chemical exergy values of the major input and output resources of bioelectricity generation from POME

Substance	Chemical formula/ composition	Density (kg/ m^3)	Standard chemical exergy ($Ex^0_{ch,i}$) (MJ/kg)
Methane	CH_4	0.66	51.81
Carbon dioxide	CO_2	1.98	0.443
Hydrogen sulfide	H_2S	1.36	23.83
POME	H_2O + CPO + sediments	400.00	0.166
Water	H_2O	1.00	0.049
Bioelectricity	–	–	1.00
Biogas	$CH_4 + H_2S + H_2O + CO_2$	–	97.12

Source Rivero and Garfias (2006), Szargut et al. (1988), Szargut (2005), Ayres and Ayres (1998)

123.5 MJ per MJ of bioelectricity produced. With about 116.3 MJ of exergy resulting as outputs (excluding CO_2 and H_2S), the overall exergy efficiency for the integrated system for biogas and bioelectricity production from POME was about 94.2 % for 1 MJ bioelectricity generated. The whole production system recorded a very low exergy destruction of 7.2 MJ resulting from entropy generation due to materials and energy dispersion during the process. The exergy efficiency could increase if possible utilization of CO_2 is considered while the capacity for electricity generation also increases. Begum and Saad (2013) have reported that the generation of electricity from POME is economically and technically sustainable based on their techno-economic assessment. Their conclusion is tantamount to the findings of this study that bioelectricity from POME is thermodynamically sustainable but still needs further improvement.

Though energy use by the anaerobic digester was highest, it recorded a negative exergy destruction (−1,040 MJ) as a result of high quality exergy of biogas (991 MJ) produced from the POME with low exergy value (33 MJ). The total input exergy was about 66 MJ compared to 1,106 MJ of useful exergy in the products. The POME (which is wastes) was, therefore, upgraded to a high quality energy value product (biogas) by about 1,040 MJ for about 155 kg of POME processed. Martin and Parsapour (2012) have also reported a similar scenario for which the exergy content of biogas produced from brewer's BSG was upgraded by 6,136 MJ for 60,000 tons of BSG processed. Comparing these results, it could be seen that biogas production from POME is of high quality in terms of exergy compared to that obtained from BSG.

However, when the biogas was purified to remove the water vapor, CO_2, and H_2S, the exergy content of the output (biomethane) was reduced to about 198 MJ. The purification unit recorded the highest exergy destruction of about 811 MJ followed by the CHP system (222 MJ). Entropy generation due to the dissipative effects of CO_2 and H_2S by the purification system could be a cause for increased exergy destruction. In appropriate process conditions and inefficient equipment design were among the factors which caused the increase in exergy destruction within the purification and CHP systems.

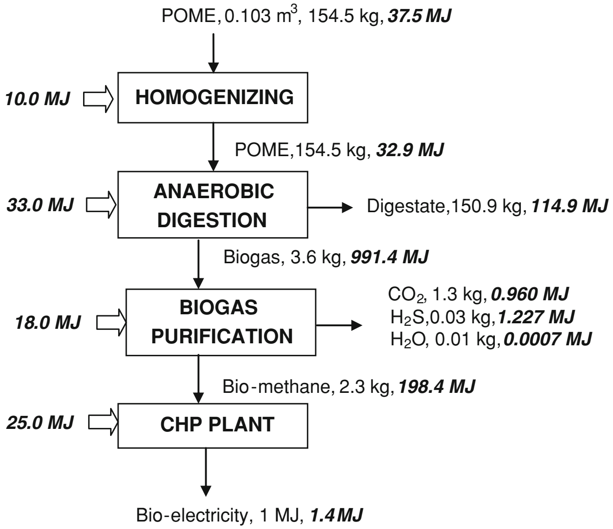

Fig. 7.8 Exergy balance for biogas and bio-electricity production from POME

7.4.6 Exergy Analysis of the Production of Palm Kernel Shells (PKS)-Derived Briquettes

Biomass briquetting is the process of densifying raw biomass into compact solid composites of various shapes and sizes using pressure and heat. Briquettes are high-energy value solid biofuels that burn with little smoke compared to biomass that are directly combusted. In order to reduce the emissions from palm oil mills' CHP plants, solid palm biomass like PKS, EFB, OPF, OPT, etc., can be converted into briquettes that can be used as boiler fuels for steam and electricity generation. In the palm oil mill where steam and bioelectricity are produced from the solid palm biomass generated as wastes, PPF is the most abundantly utilized boiler fuels. Only a small percentage of PKS generated are used as boiler fuels with insignificant or no EFB utilized. EFB contains high moisture content, which need additional pretreatment before firing in the boiler. However, most CHP plants in palm oil mills do not have these facilities and hence make use of only PPF and PKS, though EFB is a potential feedstock for bioelectricity generation.

Briquettes made from PKS are found to possess high calorific value (18–20 MJ/kg) compared to most briquettes from other sources. PKS briquettes burn with less smoke and CO_2 emissions, contain less dust and impurities, have low moisture content, and can be easily transported (risk of sparks that lead to fires are avoided) unlike gaseous and liquid biofuels. Briquettes are sulfur-free solid biofuels that burn with no generation of fly ash. PKS briquettes are low cost palm solid biofuels that can be utilized in boilers for efficient heat and power generation compared to

PPF, EFB, etc., that are fired directly in boilers for steam and bioelectricity generation.

PKS briquettes making begin with the pretreatment stage which comprises screening, drying (either by sun or flash dryer), and milling into very small sizes (in some cases, the PKS are milled to powders). Alternatively, torrefaction, pyrolysis, or carbonization can be used as a way of removing moisture from the biomass before briquetting. The method used to dry the biomass before pressing depends on the applications for which the product would be used. For instance, a piston press can be used to make briquettes that can be used for a variety of applications. The PKS after pretreatment is transported by pneumatic system to containers that are fixed to the briquetting press. Cyclones are attached for dust and solid particles collection during briquetting. Natural binder from the biomass (like lignin) binds the surfaces of the biomass together upon rise in temperature during briquetting. The briquetting process transforms the original biomass into biofuels with unique characteristics that are capable of burning efficiently. For example, screw extrusion can produce toroidal or oval-shaped homogeneous briquettes with large surface area that could burn faster and efficiently just like coal in a cogeneration plant. The production of briquettes can release significant amounts of emissions in the form of dust and particles during raw material handling, pretreatment, and pressing. The wastes generated in a briquetting plant are mainly the solid residues from the biomass used as raw material.

The main unit operations considered in this study are drying, grinding, briquette pressing, and cooling. The PKS with moisture content of about 30 % is first dried to moisture of about 10 % using a conventional oven dryer or flash dryer. Open sun drying is a cheaper alternative for drying the PKS but it is found to alter the quality of the raw material due to poor ventilation, contaminations by impurities, etc. The dried PKS are screened to remove unwanted materials before grinding. Examples of unwanted materials that may be present in the PKS before processing are stones, fibers, palm kernels, etc. In this study, the manual briquetting technology that employs the screw press type briquetting machine (commonly called the extrusion machine), was used to obtain the PKS briquettes without any binding material. The PKS briquettes were cooled in the open air to reduce its temperature before packaging. A ton of PKS briquettes is chosen as the functional unit. For the production of 1 ton PKS briquettes, about 1,002 kg of PKS is needed. The standard chemical exergies of PKS and PKS briquettes are 25.8 and 20.1 MJ/kg, respectively (obtained from Eq. 7.16). Figure 7.9 shows the exergy balance estimation for the production of briquettes from PKS.

From Fig. 7.9, the main input into the briquetting unit is the PKS with about 27,912 MJ exergy content. The product of interest is PKS briquettes, which according to Fig. 7.9, contained about 21,184 MJ exergy. This implies that PKS were degraded by 24 % in terms of exergy when they were processed into briquettes. For the production of 1 ton PKS briquettes, about 7,039 MJ of exergy was destroyed making the production process 75 % exergetically efficient. The total exergy of wastes was about 62 MJ which was contributed mainly by the impurities

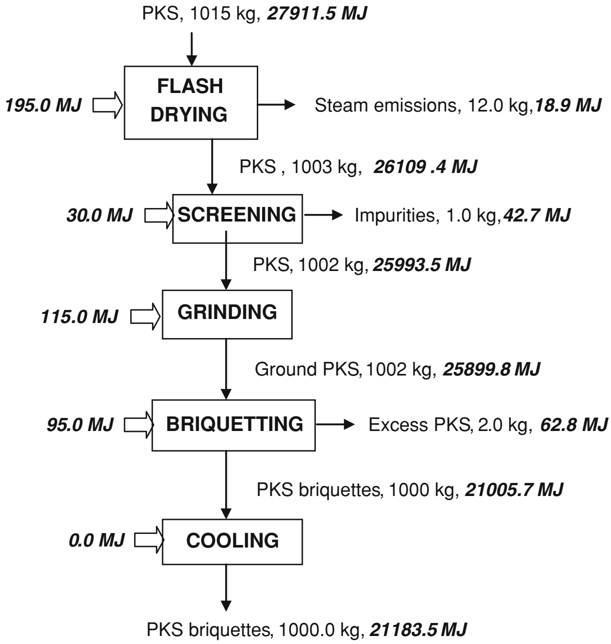
PKS, 1015 kg, 27911.5 MJ
195.0 MJ
FLASH DRYING
Steam emissions, 12.0 kg, 18.9 MJ
PKS , 1003 kg, 26109 .4 MJ
30.0 MJ
SCREENING
Impurities, 1.0 kg, 42.7 MJ
PKS, 1002 kg, 25993.5 MJ
115.0 MJ
GRINDING
Ground PKS, 1002 kg, 25899.8 MJ
95.0 MJ
BRIQUETTING
Excess PKS, 2.0 kg, 62.8 MJ
PKS briquettes, 1000 kg, 21005.7 MJ
0.0 MJ
COOLING
PKS briquettes, 1000.0 kg, 21183.5 MJ

Fig. 7.9 Exergy balance for PKS Briquetting Processes

which were part of the PKS before processing and were removed after the screening process.

However, the individual unit operations recorded exergy efficiencies higher than 80 %. On the other hand, the exergy destructions were higher for some of the units. For instance, the briquetting and drying units recorded high exergy destructions of about 4,926 and 1,978 MJ, respectively. These units used high amount of energy for processing. With about 25,995 MJ of exergy of resources that entered the briquetting unit, about 19 % was degraded during processing because of entropy generation. The briquetting press uses high amounts of energy and pressure for extrusion causing resource or matter dissipation, hence exergy destruction. Appropriate choice of process conditions and equipment design efficiency would help reduce the exergy destruction.

The cooling process was the most exergetically efficient with resource input upgrade of about 178 MJ exergy. Because an open air or natural ventilation was used to cool the briquettes, energy input was zero.

The screening and grinding processes recorded low exergy destruction of about 103 and 209 MJ, respectively, compared to the other units. Figure 7.10 shows the summary of exergy destruction distributions by the unit operations for PKS briquetting.

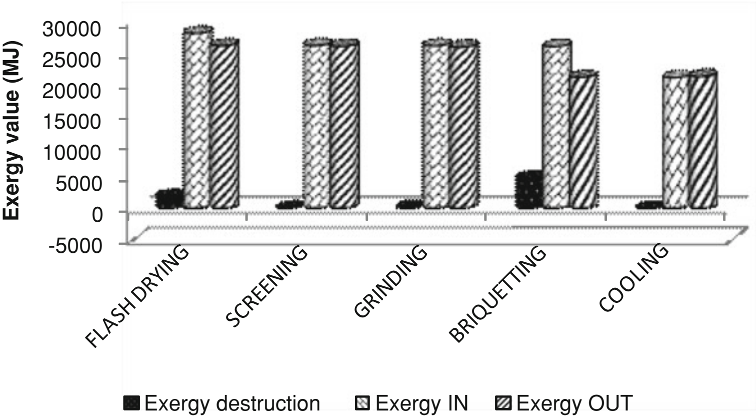

Fig. 7.10 Exergy Destructions occurring in PKS briquetting production system

7.5 General Improvement Options for Palm Biofuels Production Systems

Several authors have suggested various ways of improving the thermodynamic sustainability of biofuels production processes (Linnhoff 1983; Leites et al. 2003; Sama et al. 1989; De Swaan and Van der Kooi 1993).

Agricultural systems such as oil palm cultivation units can be improved thermodynamically by the reduction of chemical fertilizers, fossil fuels, and other input materials that have high exergy contents. The use of organic fertilizers, solar powered irrigation systems, and other best management practices (see Chap. 4, Table 4.1) for sustainable oil palm biomass production must be encouraged.

Palm oil milling processes are also found to degrade significant amounts of input exergy resulting in low efficiency of the system. The utilization of wastes like EFB, PPF, and PKS for value-added bioproducts must be the goal of all palm oil millers as this would decrease the exergy of wastes into the environment. Technically, inefficient design of equipment and processes without conformity to the sustainability standards set by the RED-RSPO, can lead to high exergy destruction, thus the need to avoid these occurrences.

For biodiesel production from palm feedstocks like CPO, PFAD, CPKO, etc., can be improved drastically by replacing the conventional distillation columns with supercritical methanol method which make use of the reactive petlyuk column (Gomez-Castro et al. 2010). This configuration is found to reduce the energy consumption by 45 % compared to conventional distillation trains because it does not present the re-mixing effect (Triantafyllou and Smith 1992), hence highly recommended for biodiesel production. This technique can be applied to bioethanol and biomethanol production units for palm biofuels production. Thermally coupled reactive distillation process for biodiesel production has been shown to be sustainable because the column uses vapor–liquid interconnections to achieve heat transfer by direct contact with the streams, hence no need for double condensers and reboilers (Gomez-Castro et al. 2008).

In a palm biofuel production system where the processes involve heat transfer (e.g., using heat exchangers, dryers, evaporators, distillation columns etc.), entropy generation becomes an important parameter to study and optimize. For streams which have the same heat capacities, the driving force (e.g., temperature, pressure, etc.) is also the same and in such situations, the driving force can be minimized (in order to minimize entropy generation leading to exergy destruction) by increasing the heat transfer area, or the overall heat transfer coefficient. This can further lead to a reduction in heat duty, especially with distillation columns, where the number of feed stages and reflux ratios are optimized. For complex systems where the driving force may keep changing, the design of the equipment plays an important role. For instance in a distillation column, the column height can be increased or the feed stage can be increased in order to approach equilibrium at one or two points.

The exergetic efficiencies of palm biofuels production systems can be improved by process adjustments such as optimization of the FFA ratio in the oils (for biodiesel production) to increase the purity and yield of the product. This can be applied to biogasoline and bioethanol production systems where the feed oils or holocellulose must be of high purity before conversion. Again, the exergy destruction due to heat loss can be minimized by reusing in-process heat, thereby minimizing the energy supply.

Also, all methanol recovery units as well as separation equipment must be optimized, i.e., reducing the reflux ratio to reduce heat duty. There is maximum exergy loss in the separation units of the plant when the temperature change is not constant (nonisothermal). This can be replaced by isothermal process equipment, e.g., with the extractive decanter. To have a realistic size of equipment and make a given process take place in finite time, there is a greater need for a minimum driving force (Leites et al. 2003). It is thus, always necessary to give allowances for the minimum potential difference while carrying out the analysis of a system with the aim of reducing the exergy loss. For the design and development of energy and exergy efficient production systems, turbulence and vorticity on entropy production in different processes as well as the influence of heat on the system and chemical composition of the inputs are vital for consideration. Also, work extraction devices such as the centrifuge should be properly designed to extract the maximum exergy contained in the product.

Input resources like catalysts, etc., have serious effects on the efficiency of the biofuels production systems. Performing the mass and heat balances makes it possible to determine whether a particular heat source and/or sink present an appropriate option for the given duty. In the distillation columns, it was observed that the irreversibility increased with recirculation or increased reflux ratio and decreased number of ideal stages.

To increase the exergy efficiency and use energy in a more rational way, renewable energy resources like solar energy, which have low emissions into the environment, may reduce the external exergy destruction. For instance, in situations where open sun drying can be used without problems, it should be an alternative to flash drying or any other means of drying using energy from non-renewable sources. Fossil fuels and electricity from fossil fuel have high exergies and must be used in low amounts. Electricity can be exploited with low exergy losses with high coefficient of performance heat equipment and pumps. Use of fossil fuels for thermal purposes must be avoided and replaced with solar energy or other possible renewable and clean means of heating. Though the exergy content of the sun's energy is high, its exploitation with even low exergy efficiencies may produce a better impact (because it is a renewable energy source) compared to fossil fuel. Fossil fuel releases more emissions into the environment upon combustion hence contributing to exergy inefficiencies but solar energy use shifts the production to more renewability or sustainability.

The thermodynamic improvement potential is, however, not directly proportional to the cost of unit operation thus the reduction of irreversibilities may not necessarily lead to lower cost of equipment. Therefore, the cost factor may render the requirement for thermodynamic perfection unattractive and ambiguous. For instance in a dryer or heat exchanger, where the irreversibility is mainly due to heat transfer, energy loss can be achieved either by increasing or reducing the temperature coefficient which may either increase or decrease the cost of production. Again, the temperature difference between the air supply and the supply temperature of the product affects the exergy consumption in the drying process. According to Keey (1978), if air recycle can be done effectively in continuous drying, the gain in thermal economy becomes worthwhile and performance of these systems can be improved effectively. This study, however, did not consider the cost aspects of the production plants since the input and output exergies can justify the thermodynamic sustainability of the plant.

7.6 Conclusion

The thermodynamic feasibility of palm biofuels production systems were assessed based on the literature values which were simulated in Aspen Plus software. Potential causes and improvement options have been discussed in this chapter for sustainable palm biofuels production. The production of palm biodiesel, bioethanol and bioelectricity from oil palm wastes would be exergetically efficient when process improvement options are critically taken into consideration.

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